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15 using same

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## SPECIFICATION

### 1. Title of the Invention

10 Resin composition and multilayer structure using  
same

### 2. Scope of Claim for Patent

(1)

A resin composition comprising 6 to 70 parts by  
15 weight of an ethylene-vinyl acetate copolymer  
hydrolyzate (A) with an ethylene content of 45 to 60 mole  
percent and a vinyl acetate component hydrolysis degree  
of not lower than 96 mole percent and 94 to 30 parts by  
weight of an ethylene-vinyl acetate copolymer  
20 hydrolyzate (B) with an ethylene content of 25 to 40 mole  
percent and a vinyl acetate component hydrolysis degree  
of not lower than 96 mole percent, said composition giving  
a melting curve showing a plurality of endothermic peaks  
as recorded using a differential scanning calorimeter.

25 (2)

A multilayer structure comprising a polypropylene  
layer at least on one side of a layer made of a resin

composition comprising an ethylene-vinyl acetate copolymer hydrolyzate (A) with an ethylene content of 45 to 60 mole percent and a vinyl acetate component hydrolysis degree of not lower than 96 mole percent and  
5 an ethylene-vinyl acetate copolymer hydrolyzate (B) with an ethylene content of 25 to 40 mole percent and a vinyl acetate component hydrolysis degree of not lower than 96 mole percent, said composition giving a melting curve showing a plurality of endothermic peaks as recorded  
10 using a differential scanning calorimeter, the tensile tension ratio of the layer of the resin composition (A) + (B) to the polypropylene layer being not higher than 5.

(3)

15 The multilayer structure according to Claim 2, wherein (A) and (B) satisfy the following conditions (I) to (III):

$$1 \leq E' (B) / E' (A) \quad (I)$$

$$E' (A) \leq 10^9 \text{ dyne/cm}^2 \quad (II)$$

20  $0.05 \leq MI (A) / MI (B) \leq 20 \quad (III)$

where:

$E' (A)$  = dynamic viscoelasticity of A at  
heating/drawing/forming temperature  $-10^\circ \text{C}$ ,  
 $\text{dyne/cm}^2$

25  $E' (B)$  = dynamic viscoelasticity of B at  
heating/drawing/forming temperature,  $\text{dyne/cm}^2$

$MI (A)$  = melt index of A at  $190^\circ \text{C}$  under a load of 2160

g, g/10 min

MI(B) = melt index of B at 190 °C under a load of 2160

g, g/10 min

(4)

5           A multilayer structure according to Claim 3,  
wherein the following conditions (I') to (III') are  
satisfied:

$$10 \leq E'(B)/E'(A) \quad (I')$$

$$E'(A) \leq 8 \times 10^8 \text{ dyne/cm}^2 \quad (II')$$

10            $0.06 \leq MI(A)/MI(B) \leq 18 \quad (III')$

### 3. Detailed Description of the Invention

#### A. Industrial Field of Utilization

          This invention relates to an ethylene-vinyl acetate  
copolymer hydrolyzate (hereinafter referred to as EVOH)  
15 resin composition causing no pinhole formation, cracking,  
partial thickness irregularities or the like during  
high-speed drawing or stretching procedure under heating,  
in particular, and, further, excellent in gas barrier  
properties, and to a multilayer structure composed of  
20 a layer of the resin composition and a polypropylene  
(hereinafter referred to as PP) layer and producible by  
drawing with heating, in particular high-speed drawing  
with heating.

#### B. Prior Art

25           Nowadays EVOH is recognized to be effective in such  
field of use as packaging films for foodstuff, in  
particular foodstuffs for which barrier properties

against oxygen are required, and for other products whose flavors are required to be retained, for instance. However, films produced from a single EVOH species have drawbacks, namely they are lacking in toughness and show  
5 no effective barrier properties against water vapor.

For alleviating these drawbacks, such films are used in many cases in the form of multilayer structures resulting from lamination of polypropylene with at least one of various heat sealant layers, typically ionomers  
10 and ethylene-vinyl acetate copolymers.

Meanwhile, when multilayer structures (films, sheets, parisons) comprising an EVOH layer and a polypropylene layer are subjected to secondary processing to produce containers, for instance, in  
15 particular when draw forming is carried out at a temperature not exceeding the melting point of EVOH, pinhole formation, cracking and local thickness irregularities among others occur frequently in the EVOH layer and, as a result, the oxygen barrier properties  
20 of the formed containers markedly deteriorate. Further, their appearance becomes damaged, and the containers can no longer be used for packaging foodstuffs and the like.

Therefore, heretofore, measures for preventing pinhole formation, cracking and like phenomena from  
25 occurring in the EVOH layer on the occasion of drawing with heating have been investigated, for example the addition of various plasticizers to EVOH (JP-A No.

88067/1978, JP-A No. 20345/1984) and the blending with polyamide type resins (JP-A No. 141785/1977, JP-A No. 154755/1983, JP-A No. 36412/1983). In any case, however, the effects are not fully satisfactory.

5           Further, JP-A No. 101182/1977 describes the production of multilayer laminated containers excellent in barrier properties and adhesiveness by lamination of a layer of a mixture resulting from compounding 95 to 99.5 parts by weight of an EVOH species having an ethylene  
10 content of not higher than 50 mole percent and a degree of hydrolysis of not lower than 96 mole percent with 0.5 to 5 parts by weight of an EVOH species having an ethylene content of 50 to 90 mole percent and a degree of hydrolysis of 50 to 95 mole percent with a polyolefin layer at least  
15 on one side of the EVOH layer. However, it is difficult to prevent minute pinhole formation, cracking, thickness irregularities and so forth from occurring even when such an EVOH mixture layer as described in the publication cited above and a PP layer to lamination and drawing with  
20 heating. This is evident from the results of some comparative examples described later herein.

          Therefore, it is one of the important problems to develop an EVOH species showing good molding/processing characteristics such as minute pinholes, cracking and  
25 thickness irregularities on the occasion of drawing with heating, in particular high-speed drawing with heating, of EVOH layer-polypropylene layer laminates.

### C. Problems Which the Invention is to Solve

While EVOH has excellent characteristics, as mentioned above, EVOH-polypropylene laminates, when subjected to secondary processing into containers or the like, encounter cracking, pinhole formation and local thickness irregularities, among others, in the EVOH layer, with the result that their gas barrier properties markedly deteriorate.

Further, the moldings become poor in appearance and can no longer be used as food packaging containers.

Therefore, the present inventors made intensive investigations in an attempt to develop an EVOH composition for multilayer containers having high-level gas barrier properties which composition makes it possible to inhibit the occurrence, in the EVOH layer, of cracking, pinhole formation, local thickness irregularities and so forth on the occasion of secondary processing of laminates thereof into containers or the like, without sacrificing the good gas barrier properties of EVOH. As a result, they have now completed the present invention.

### D. Means for Solving the Problems

The present invention relates to a resin composition comprising an ethylene-vinyl acetate copolymer hydrolyzate (A) with an ethylene content of 45 to 60 mole percent and a vinyl acetate component hydrolysis degree of not lower than 96 mole percent and

an ethylene-vinyl acetate copolymer hydrolyzate (B) with an ethylene content of 25 to 40 mole percent and a vinyl acetate component hydrolysis degree of not lower than 96 mole percent, the composition giving a melting curve showing a plurality of endothermic peaks as recorded using a differential scanning calorimeter, and to a multilayer structure comprising a polypropylene layer at least on one side of a layer made of the resin composition, with the tensile tension ratio of the layer of the resin composition (A) + (B) to the polypropylene layer being not higher than 5.

#### E. More Detailed Description of the Invention

When various sheets comprising a polypropylene (PP) layer or layers bonded, via an adhesive resin, to an EVOH layer on one side or each side of the EVOH layer are prepared and subjected to secondary processing for shaping including reheating and drawing procedures and the resulting containers are evaluated for appearance and measured for gas barrier properties, it is possible to judge the superiority or inferiority in the moldability/processability and gas barrier properties of the EVOH layer. Therefore, the present inventors blended various plasticizers, polymers and so forth with EVOH, followed by evaluation of the moldability/processability and gas barrier properties of the EVOH. As a result, EVOH compositions prepared by blending 5 to 30 parts by weight of a polyamide or the



like with EVOH at first seemed to be capable of giving better moldings without the occurrence of cracking or unevenness on the occasion of thermoforming as compared with EVOH compositions prepared by blending with glycol type or amide type plasticizers or polyethylene species, ethylene-vinyl acetate types, and maleic acid modifications of these. However, upon measurement of the O<sub>2</sub> gas barrier properties of the containers produced therefrom, it was found that their gas barrier properties were worse than those of the original sheets and, to make matters worse, the measured values greatly varied from container to container and, with some containers, the barrier properties were found to have fallen to 1/10 to 1/50 levels. This tendency became more significant in particular when the rate of drawing under heating was increased, when the thickness of the EVOH composition layer was increased or when the draw ratio was increased. Thus, their reliability as gas barrier containers is highly questionable.

Therefore, the present inventors made further intensive investigations and, as a result, found that when a resin composition prepared by compounding together an EVOH species (A) with an ethylene content of not lower than 45 mole percent and an EVOH species (B) with an ethylene content of not higher than 40 mole percent in a specific mixing ratio gives a melting curve showing a plurality of endothermic peaks as measured by means

of a differential scanning calorimeter, stretched multilayer structures good in appearance can be obtained, independently of the rate of drawing, by laminating a PP layer on at least one side of a layer of such resin composition; in addition, the stretched multilayer structures show less deterioration in gas barrier properties with narrower variations in measured values.

The EVOH (A) to be used in the practice of the invention is an ethylene-vinyl acetate hydrolyzate with an ethylene content of 45 to 60 mole percent, preferably 45 to 55 mole percent, and a vinyl acetate component hydrolysis degree of not lower than 96 mole percent. Ethylene contents lower than 45 mole percent are undesirable since cracking and pinhole formation readily occur on the occasion of container forming and, further, the measured values of gas barrier properties are variable. On the other hand, ethylene contents exceeding 60 mole percent are also unacceptable since, then, the gas barrier properties deteriorate and the performance becomes insufficient for use as gas barrier containers. EVOH species having a vinyl acetate component hydrolysis degree lower than 96 mole percent are not only insufficient in gas barrier properties but also are poor in thermal stability and undergo gelation in the step of film formation; hence they are undesirable. A preferred hydrolysis degree is not lower than 98 mole percent.

On the other hand, the other EVOH (B) is an EVOH species with an ethylene content of 25 to 40 mole percent and a vinyl acetate component hydrolysis degree of not lower than 96 mole percent, preferably not lower than 98 mole percent. If the ethylene content of (B) is lower than 25 mole percent, the moldability will be insufficient and, if it is above 40 mole percent, the gas barrier properties, too, will become insufficient. If the hydrolysis degree of (B) is lower than 96 mole percent, the gas barrier properties will be insufficient.

It is important that the resin composition comprising EVOH species (A) and (B) gives a melting curve having a plurality of endothermic peaks as measured using a differential scanning calorimeter (scanning speed 10 °C/minute).

Now, as regards the mixing ratio (weight ratio) between the EVOH (A) and EVOH (B), the ratio A/B is 6/94 to 70/30. Mixing ratios  $A/B < 9/94$  are unacceptable since cracking, irregularities and pinhole formation are readily encountered and, further, the variations in gas barrier properties are great. On the other hand, in the case of  $A/B > 70/30$ , local thickness irregularities are encountered in the step of container forming and are unfavorable from the appearance viewpoint. A preferred range is  $7/93 \leq A/B \leq 45/55$ .

In the practice of the invention, it is preferred that the EVOH species (A) and (B) satisfy the following

conditions:

$$1 \leq E'(B)/E'(A) \quad (I)$$

$$E'(A) \leq 10^9 \text{ dyne/cm}^2 \quad (II)$$

$$0.05 \leq MI(A)/MI(B) \leq 20 \quad (III)$$

5 where:

$E'(A)$  = dynamic viscoelasticity of A at  
heating/drawing/forming temperature  $-10^\circ\text{C}$ ,  
 $\text{dyne/cm}^2$

$E'(B)$  = dynamic viscoelasticity of B at  
10 heating/drawing/forming temperature,  $\text{dyne/cm}^2$

$MI(A)$  = melt index of A at  $190^\circ\text{C}$  under a load of 21690  
g, g/10 min

$MI(B)$  = melt index of B at  $190^\circ\text{C}$  under a load of 2160  
g, g/10 min

15 The dynamic viscoelasticity is greatly influenced  
by the ethylene content and hydrolysis degree, among  
others, of EVOH and, when  $E'(A) > 10^9 \text{ dyne/cm}^2$ , cracking  
and pinhole formation readily occur during container  
forming and the measured values of gas barrier properties  
20 are unfavorably varied. Further,  $E'(B)$  is preferably  
not higher than  $10^{13} \text{ dyne/cm}^2$ . When the melt index ratio  
is  $MI(A)/MI(B) > 20$  or  $MI(A)/MI(B) < 0.05$ , cracking and  
pinhole formation readily occur during container forming  
and the variations in gas barrier properties also become  
25 great probably due to failure of dispersed particles to  
become minute in the EVOH (A)-EVOH (B) blend, resulting  
in nonuniform admixture. Here, the  $MI(A)$  and  $MI(B)$  are

selected within the range of 0.1 to 20 g/10 minutes, preferably 1 to 15 g/10 minutes. As regards the dynamic viscoelasticity, when  $E'(B)/E'(A) < 1$ , local thickness irregularities are caused in the step of container forming and they are unfavorable from the appearance viewpoint.

Preferred ranges of the above-mentioned (I) to (III) are as follows:

$$\begin{array}{ll} 10 \leq E'(B)/E'(A) & (I') \\ E'(A) \leq 8 \times 10^8 \text{ dyne/cm}^2 & (II') \\ 0.06 \leq MI(A)/MI(B) \leq 18 & (III') \end{array}$$

As for the method of blending EVOH (A) and EVOH (B), the method is not particularly restricted but may comprise, for example, dry blending the EVOH species (A) and (B), followed by pelletizing and drying in a Banbury single-screw mixer or twin-screw mixer, for instance. In case of nonuniform blending or formation/inclusion of a gel fraction or stones, breaking of the EVOH blend layer or occurrence of irregularities is likely.

Therefore, in blending with heating using an extruder, it is desirable that an extruder high in degree of mixing be used and the hopper opening be sealed with  $N_2$  and the extrusion be carried out at relatively low temperatures.

On the other hand, in blending these, one or more of other additives (various resins, antioxidants, plasticizers, colorants, etc.) can optionally be used at addition levels at which the effects of the invention

will not be sacrificed. In particular, the addition of 0.01 to 1% by weight of a hydrotalcite compound, a hindered phenol compound and/or a hindered amine compound is appropriate as a measure for thermally stabilizing the resin and preventing gel formation.

The EVOH composition of the invention can be molded into arbitrary shaped articles such as films, sheets, tubes and bottles by the melt molding technique or compression forming technique well known in the art. Since, however, marked characteristics can be acquired by lamination of the composition with a PP layer, as mentioned above, an explanation is given below in this respect.

The PP species to be used in the practice of the invention is not particularly restricted but includes homopolymer polypropylene, block copolymer polypropylene or random copolymer polypropylene with ethylene or the like and, further, blends of the resins mentioned above. It is also possible to incorporate another thermoplastic resin (e.g. another polyolefin such as polyethylene) in these PP species.

As the method of obtaining multilayer structures, there may be mentioned the method comprising obtaining laminates from the EVOH composition and PP via an adhesive resin by extrusion lamination, dry lamination, coextrusion lamination, coextrusion sheet forming (feed block or multimanifold technique), coextrusion pipe

forming, coinjection, or various solution coating techniques, for instance, and subjecting the laminates to reheating and drawing procedures within a temperature range not higher than the melting point of PP using a vacuum pressure deep draw forming machine or a biaxial draw blow forming machine or the like (SPPF forming), the melt forming method which is carried out at above the melting point of PP, the method submitting the above-mentioned laminates (sheets or films) to a biaxial machine for heating and drawing and, further, the method subjecting the EVOH and PP to coinjection biaxial drawing.

As for the thickness constitution of the multilayer structure, good shaped articles are obtained from those multilayer structures in which the tensile tension ratio of the EVOH layer to the PP layer at the heating/draw molding temperature is not higher than 5, preferably not higher than 1. If the tension ratio is higher than 5, cracking, irregularities and the like unfavorably tend to occur with ease even in the EVOH composition. Here, the tensile tension of the PP layer in the multilayer structure is the value at 100% elongation of the multilayer structure before drawing with heating as measured at the same temperature as the heating/drawing/forming temperature at a draw rate of 50 mm/minute with a chuck distance of 50 mm, and the tensile tension of the EVOH layer is the value measured

for the single EVOH layer composed of (A) and (B) under the same conditions as mentioned above. It is also possible to subject the multilayer structure after drawing with heating to hot pressing, release the same from drawing and, after restoring the condition before drawing with heating, measure such tensile tensions under the same conditions as mentioned above.

As for the multilayer structure constitution, there may be mentioned, as typical examples, the constitutions EVOH composition layer/adhesive resin layer/PP layer and PP layer/adhesive resin layer/EVOH composition layer/adhesive resin layer/PP layer. Here, the adhesive resin is not particularly restricted but may be any of those draw-formable at below the melting point of EVOH and capable of bonding together the EVOH composition layer and PP layer. As preferred ones, there may be mentioned polyolefins (e.g. polyethylene, polypropylene) modified by addition or grafting of an ethylenically unsaturated carboxylic acid or the anhydride thereof (e.g. maleic anhydride), ethylene-vinyl acetate copolymers, and ethylene-acrylic acid ester (e.g. methyl ester, ethyl ester) copolymers, among others.

In the practice of the invention, the multilayer structure drawn or stretched with heating is a container such as a cup or bottle or a sheet- or film-like article obtained by drawing with heating as mentioned above, and



the heating may be any method for allowing the multilayer structure to stand at a temperature necessary for drawing with heating for a predetermined period of time so that the multilayer structure may be made thermally almost  
5 uniform and, from the operability viewpoint, the method comprising heating with any of various heaters for attaining temperature uniformity is preferred. The heating temperature is selected within the range of 110 to 230 °C, preferably within the range of 120 to 210 °C.  
10 The heating operation may be carried out simultaneously or prior to drawing. The term "drawing (stretching)" means an operation for forming the thermally uniformly heated multilayer structure uniformly into containers, cups, sheets or films by means of chucks or plugs or by  
15 vacuum pressure forming or blowing, for instance, and the stretching may be either uniaxial or biaxial (simultaneous or successive). The draw ratio and draw rate (speed) can be properly selected according to the intended purpose. In the present invention, the  
20 "high-speed drawing" means the method of uniformly forming containers or film-like articles at a high draw rate or speed (area drawing ratio (%)/minute) of not lower than  $5 \times 10^5\%$ /minute. It is not always necessary that the shaped articles thus obtained be oriented ones.

25 As for the draw ratio, an area draw ratio of 3 times or higher is expected to be markedly effective in the practice of the invention. A preferred draw ratio is 3

to 60 times. The upper limit to the draw ratio is about 70 times. At ratio levels exceeding 70 times, the drawing of PP becomes difficult and, on the multilayer structure level, too, good ones can hardly be obtained.

5 In the practice of the invention, the water content in the EVOH composition layer, which is a constituent of the multilayer structure, to be drawn with heating is not particularly restricted but is preferably 0.01 to 10%, more preferably 0.01 to 5%. The method of  
10 recovering the scraps, such as trims and defective containers, is not particularly restricted. Available are, for example, the method comprising grinding the scraps, drying the ground mass if they are moist, and dry blending the same with the raw material PP resin,  
15 the method comprising pelletizing the ground scraps and dry blending the pellets with the raw material PP resin, and the method comprising blend pelletizing the ground scraps and the raw material PP resin. The blending ratio between the raw material PP and the scraps is selected  
20 according to the molding conditions since such abnormalities as thickness irregularities, unevenness, cracking and whitening tend to occur more easily in the step of drawing with heating as the proportion of scraps increases. Generally, however, the scraps are blended  
25 at addition levels of about 2 to 40%. At this time, it is sometimes desirable that a plurality of species selected from among maleic anhydride-modified

polyolefins, metal soaps, hydrotalcite compounds and the like be added to improve the dispersibility and thermal stability and suppress the occurrence of such abnormalities as mentioned above.

5           The multilayer structure of the invention as thus obtained after high-speed drawing with heating is free of pinholes, cracks or thickness irregularities in the EVOH composition layer and thus shows very good gas barrier properties, with almost no substantial  
10 variations therein, and is effective for use as a very good food packaging container or a container required to have a flavor-retaining ability.

          The following examples illustrate the present invention in further detail. They are, however, by no  
15 means limitative of the scope of the invention.

#### F. Examples

##### Example 1

          The dynamic viscoelasticity ( $E'_{150\text{ }^{\circ}\text{C}}$ ) of an EVOH species (A) with an ethylene content of 50 mole percent, a hydrolysis degree of 99.4 mole percent and a melt index (MI) ( $190\text{ }^{\circ}\text{C}$ ) of 16 g/10 minutes as measured using Vibron (product of Toyo Baldwin, measuring frequency 110 Hz) was not higher than  $10^8$  dyne/cm<sup>2</sup>. On the other hand, the dynamic viscoelasticity ( $E'_{140\text{ }^{\circ}\text{C}}$ ) of an EVOH species (B)  
20 with an ethylene content of 32 mole percent, a hydrolysis degree of 99.6 mole percent and a melt index ( $\text{MI}_{190\text{ }^{\circ}\text{C}}$ ) of 1.5 g/10 minutes was  $3 \times 10^9$  dyne/cm<sup>2</sup>. The EVOH (A)  
25

and EVOH (B) were blended together in a weight ratio A/B = 20/80 and the blend was pelletized by extrusion at 200 °C under N<sub>2</sub> using a twin-screw vented extruder (40 φ). The pellets obtained were dried at 80 °C for 8 hours.

5 Using these pellets, a sheet was produced on a feed block type three-resin five-layer coextrusion machine. As for the sheet constitution, both the outermost layers were each 800-μ-thick polypropylene (Mitsubishi Noblen MA-6) layer, each adhesive resin layer (Mitsubishi Yuka Modic

10 P-300F) had a thickness of 50 μ, and the innermost layer (middle) was a 50-μ-thick layer made of the above EVOH composition. Upon measurement of the above pellets by DSC (scanning speed 10 °C/min), two endothermic peaks (150 °C, 183 °C) were observed. The sheet obtained was

15 subjected to tensile tension measurement at 150 °C (pulling rate 50 mm/min, chuck distance 50 mm); the tension of the polypropylene layer at 100% elongation was 1.0 kg/15 mm width. The tension of the single EVOH layer (50 μ) under the same conditions was 0.2 kg/15 mm

20 width. Thus, the EVOH layer/polypropylene layer tensile tension ratio was 0.2. The sheet was subjected to thermoforming on a vacuum pressure molding machine (draw rate  $9 \times 10^6\%$ /min, draw ratio 1, area draw ratio 7-fold) at 150 °C (SPPF forming). The shaped articles obtained

25 were good in transparency and appearance and showed no cracks or thickness irregularities. The gas barrier performance of these containers was measured at 20 °C

and 65% RH using a Mocon model 10/50 apparatus. The oxygen permeability was  $0.7 \text{ cc} \cdot 20 \text{ } \mu/\text{m}^2 \cdot 24 \text{ hr} \cdot \text{atm}$  and, thus, the gas barrier performance was very good and, in addition, the dispersion ( $R = \text{maximum value} - \text{minimum value}$ ) of the measured values for 10 samples was as small as  $0.1 \text{ cc} \cdot 20 \text{ } \mu/\text{m}^2 \cdot 24 \text{ hr} \cdot \text{atm}$ ; the containers were good barrier containers.

#### Comparative Example 1

The procedure of Example 1 was followed in the same manner except that the EVOH (A)/EVOH (B) blending ratio was changed to 4/94 by weight.

As a result, a large number of cracks and thickness irregularities were found and, as for the gas barrier properties, the permeability was as high as  $5 \text{ cc} \cdot 20 \text{ } \mu/\text{m}^2 \cdot 24 \text{ hr} \cdot \text{atm}$ , hence the containers were not fit for use.

#### Comparative Example 2

The procedure of Example 1 was followed in the same manner except that a single EVOH species (single peak in DSC,  $\text{MI}_{190} \text{ } ^\circ\text{C}$  4.0 g/10 min) having the same ethylene content as the average ethylene content (36 mole percent) of the EVOH (A)-EVOH (B) blend (20/80) was used. As a result, a large number of cracks and thickness irregularities were found and the containers were not fit for use.

#### Example 2

The dynamic viscoelasticity ( $E'_{190} \text{ } ^\circ\text{C}$ ) of an EVOH species (A) with an ethylene content of 47 mole percent,

a hydrolysis degree of 99.4 mole percent and a melt index ( $MI_{190^{\circ}C}$ ) of 10 g/10 minutes was not higher than  $10^8$  dyne/cm<sup>2</sup>. On the other hand, the dynamic viscoelasticity ( $E'_{180^{\circ}C}$ ) of an EVOH species (B) with an ethylene content of 27 mole percent, a hydrolysis degree of 99.6 mole percent and a melt index ( $MI_{210^{\circ}C}$ ) of 2.8 g/10 minutes was  $10^9$  dyne/cm<sup>2</sup>. The EVOH (A) and EVOH (B) were compounded together in a weight ratio of A/B = 10/80 and the blend was pelletized and the pellets were used for sheet formation in the same manner as in Example 1. Upon DSC measurement of the pellets (scanning speed 10 °C/min), two endothermic peaks (198 °C, 175 °C) were observed. The sheet obtained was subjected to tensile tension measurement at 190 °C; the tension of the polypropylene layer at 100% elongation was 0.2 kg/15 mm width and the tension of the single EVOH layer (50 μ) under the same conditions was 0.1 kg/15 mm width. Thus, the EVOH layer/polypropylene layer tensile tension ratio was 0.5. The sheet was subjected to thermoforming on a vacuum pressure molding machine (draw rate  $6 \times 10^8\%$ /min, draw ratio 1.8, area draw ratio 12-fold) at 190 °C. The shaped articles obtained showed no cracks or unevenness or thickness irregularities and had a good appearance. The gas barrier performance of these containers was good, namely the permeability was  $0.4 \text{ cc} \cdot 20 \mu/\text{m}^2 \cdot 24 \text{ hr} \cdot \text{atm}$  (20 °C, 65% RH), and the dispersion (R) of the measured values for 10 samples was as small as 0.1; the containers were

good barrier containers.

#### Comparative Example 3

The procedure of Example 2 was followed in the same manner except that an EVOH species with an ethylene  
5 content of 47 mole percent, a hydrolysis degree of 99.4 mole percent and a melt index ( $MI_{190}^{\circ C}$ ) of 60 g/10 minutes was used in lieu of the EVOH (A). As a result, the shaped containers showed a large number of small thickness irregularities and were not fit for use from the  
10 appearance viewpoint.

#### Comparative Example 4

The procedure of Example 1 was followed in the same manner except that an EVOH species (B) with an ethylene  
content of 42 mole percent, a hydrolysis degree of 99.6  
15 mole percent and a melt index ( $190^{\circ C}$ ) of 20 g/10 minutes was used in lieu of the EVOH (B). On that occasion, the pellets of the EVOH (A)-EVOH (B) blend were subjected to DSC measurement, upon which apparently one single endothermic peak was observed. As a result, minute  
20 irregularities (thickness irregularities) were observed on the shaped containers, and the dispersion (R) of the gas barrier property measurement values was as wide as  $1.2 \text{ cc} \cdot 20 \mu / \text{m}^2 \cdot 24 \text{ hr} \cdot \text{atm}$ ; hence, the containers were not fit for use.

#### 25 Example 3

The trims and defective containers resulting from Example 1 were ground and the ground resin was blended,

in an amount of 10% by weight, with polypropylene (MA-6). The procedure of Example 1 was followed using the polypropylene containing the recovered resin. As a result, the shaped articles obtained showed a good appearance and good gas barrier properties ( $0.7 \text{ cc} \cdot 20 \mu/\text{m}^2 \cdot 24 \text{ hr} \cdot \text{atm}$ ) and the dispersion (R) was very narrow, namely  $0.1 \text{ cc} \cdot 20 \mu/\text{m}^2 \cdot 24 \text{ hr} \cdot \text{atm}$ ; the containers were good barrier containers.

#### Comparative Example 5

The procedure of Example 1 was followed in the same manner except that an EVOH species with an ethylene content of 52 mole percent, a hydrolysis degree of 70 mole percent and a melt index ( $\text{MI}_{190}^{\circ\text{C}}$ ) of 15 g/10 minutes was used as the EVOH (A) and that the EVOH (A)/EVOH (B) mixing ratio was changed to 4/96. The shaped articles obtained showed a large number of pimple-like spots and the EVOH layer showed minute cracks around the spots. As a result, the permeability indicative of gas barrier properties was as high as  $23 \text{ cc} \cdot 20 \mu/\text{m}^2 \cdot 24 \text{ hr} \cdot \text{atm}$ ; the containers were thus not fit for use.

#### G. Effects of the Invention

The multilayer structure of the invention shows a very few cracks and thickness irregularities and is very excellent in gas barrier properties, with the variations in gas barrier properties being very small.